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Polypyrrole and Thienyl End Capped Polysulfone Copolymers by Iron (III) Chloride

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Abstract

This study presents synthesis of novel block copolymers of thienyl end capped polysulfone and polypyrrole via chemical oxidative polymerization by iron (III) chloride. Polysulfone is synthesized from bisphenol and bis (p-chlorophenyl) sulfone in presence of potassium carbonate. Polysulfone (PSU) was reacted with 2-thiophenecarbonyl chloride in order to synthesize a macromonomer containing thienyl end-group (PSU-ThC). Then copolymers of PSU-ThC and pyrrole were synthesized by chemical oxidative polymerization using iron (III) chloride as an oxidant. The synthesized block copolymers (PSU-ThC-b-PPy) were characterized by spectroscopic analysis and the electrical conductivities were investigated with 4-point probe technique. The obtained samples were also characterized morphologically by Scanning Electron Microscope (SEM).

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Keywords: End-capped polymer; polysulfone; polypyrrole; iron (III) chloride.

1. Introduction

Polysulfone (PSU) is one of the amorphous engineering thermoplastic that can be used for special engineering purposes. PSU's backbone contains the sulfone groups (SO2) in the main chain along with a variety of aromatic

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constituents like ether or iso-propylidene groups (Summers, G. J., Ndawuni, M. P., & Summers, C. A., 2001). PSU is widely used as a specialty engineering plastic since its great thermal stability, durability, high tensile strength, good chemical stability and pressure resistance (Anadão, P., Sato, L. F., Wiebeck, H., & Valenzuela-Díaz, F. R. 2010; Richards, H. L., Baker, P. G. L., & Iwuoha, E. 2012). It has many application areas such as medical, electric-electronic and membranes. But especially it is widely used in membrane production.

Polypyrrole (PPy) is a conductive polymer, which has good electrical conductivity, high air stability. Nowadays polypyrrole has become important material since its wide range of technological applications in several application fields like secondary batteries, electro-chromic display devices, sensors, light-emitting diodes, capacitors, and enzyme electrodes and also membranes (Shimizu, A., Yamaka, K., & Kohno, M. 1988 - Selampinar, F., Akbulut, U., Ozden, M.Y., & Toppare, L., 1997).

There are many studies about conductive membranes, these having various usage areas such as seperation, biomedical field, electronic, electrochemical devices, and fuel cells (Loh, I. H., & Moody, R. A., 1990- Hu, W., Chen, S., Liu, Z. Y. L., & Wang, H., 2011). But poor production and processibility there are also some new studies about PSU/PPy composite membranes where are used as a conductive membrane (Bhattacharya, A., Mukherjee, D.C., Gohil, J. M., Kumar, Y., & Kundu, S., 2008, Muscalu, C., David, R., Garea, S.A., Nechifor, A.C., Vaireanu, D.I., Voicu, S.I., & Nechifor, G., 2009). The combination of PSU and PPy brings better material properties to the final product. Not only both polymer's properties are gained but also disadventages of their poor mechanical specialties are improved.

In this study, it is aimed to produce a new conductive membrane material from polysufone and polypyrrole copolymer with the addition of sepiolite as a nanoparticle to improve the material properties. The nanocomposite of polysulfone and sepiolite are synthesized by in-situ methode and 1% sepiolite is used. After that the end group of PSU/Sepiolit nanocomposite is functionalyzed by thiophene-2-carboxylic acid chloride for the purpose of copolymerization with pyrrole. Copolymers of pyrrole and nanocomposite are synthesized by using $Fe(III)Cl_3$. The FTIR and SEM analyses of PPy-PSU copolymers are done.

2. Methodology

In this study it is aimed to synthesis a new membrane material consist of PSU-Ppy copolymer. In order to achieve this goal first polysulfone is synthesized by polycondensation, then its end groups are functionalized by thiophene-2-carboxylic acid chloride. Afterwards pyrrole monomer and thiophene-2-carboxylic acid chloride end capped PSU are polymerized together by redox polymerization with iron (III) chloride.

2.1. Materials

Bisphenol-A, 2-thiophenecarbonyl chloride and p-chlorophenylsulfone are from Sigma Aldrich. Pyrrole (Py), hydrochloric acid (Sigma Aldrich), sodium bicarbonate (Tekkim), dichloromethane (Merck), pyridine (Analar) and iron (III) Chloride (FeCl3), dimethyl acetamide (Sigma-Aldrich), toluene (Alfa Aesar), prydine (Analar) are all reagent-grade chemicals of the highest purity, so they were used without further purification.

For solution mixing, Heidolph magnetic stirrer (MR Hei-Standart) was used. Fourier transform infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrum One B spectrometer. SEM images taken by The Philips XL30 ESEM-FEG/EDAX system: Microscopy & Microanalysis Lab.

2.2. Polysulfone Synthesis

In this study it is considered to synthesized polysulfone with lower molecular weight comparing with commercial PSU, to achieve its end-group functionalization and via its copolymerization in the later steps. In order to obtain PSU-4000, bisphenol A and p-chlorophenylsulfone are taken 6:5 molar ratio respectively. After that dried potassium carbonate is taken 1:1 ratio with p-chlorophenylsulfone. All those materials are weighted and added into a 3 necked round bottom flask. Dimethyl acetamide (DMAC) and 50 ml toluene mixture is added to the reaction flask as solvent medium. One of the three necks of the flask is fitted with a condenser, other is fitted nitrogen inlet, and the last neck

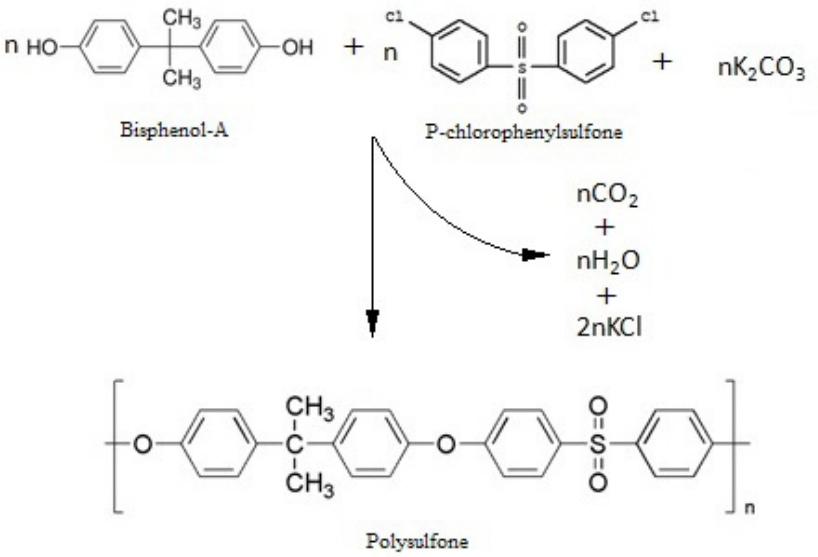

Fig. 1. Polycondensation of PSU

fitted with a Dean and Stark trap for the removal of the water by-product from the reaction medium. The reaction proceeds under reflux at 150°C for 12h in the N_2 atmosphere. The reaction mechanism shown in Fig. 1.

After the reaction, the reaction flask leaved to cool for 2 hours at room temperature. The reaction mixture is filtered to remove the salts occurred as by-product. Filtered polymer solution is poured into methanol and water mixture, prepared with 4:1 volume ratio respectively. The precipitated polymer is filtered, and washed several times with methanol-water solution to remove the remaining salts and impurities. Finally, the polymer dried in a vacuum oven at 65°C.

2.3. End Group Functionalization of PSU

The end groups of the polysulfone was reacted with 2-thiophenecarbonyl chloride (Th-CCl) in order to synthesize a macromonomer containing thienyl end-group. The reaction is proceeded in the N_2 atmosphere at 0^oC for 24 hours. For this reaction a three necked 200ml balloon, a mechanical mixer (Heidolph RZR 2020), a dropping funnel, condenser, N_2 adapter and ice bath are used. 3g of PSU is weighed and added in to the reaction balloon, then chloroform (Merck) is taken as the solvent medium with the ratio of 35ml for 10g PSU. Afterwards prydine (Analar) is taken into the balloon, in order to eliminate chloride part, which comes from 2-thiophenecarbonyl chloride, with the estimated amount by the Equation 1.

$$n_{Prydine} = 1.2 * n_{Tyofen} \quad (1)$$

Thiophene-2-carboxylic acid chloride amount is calculated according to the Equation 2 and added into the dropping funnel with 5ml chloroform.

$$n_{Tiyofen} = 2.2 * n_{PSU} \quad (2)$$

Reaction balloon is placed on the ice bath, to prevent a violent reaction may be happened between thiophene-2-carboxylic acid chloride and PSU. Then mechanic stirrer is assembled with the balloon. One of the empty necks is

attached with the condenser and the other neck is connected with N_2 adaptor and stirrer is switched on. For an hour N_2 gas is passed through the reaction medium. Latter N_2 adaptor is ejected and dropping funnel is attached with the neck. Dropping rate is adjusted to finish its content in 30min. After all the material in the funnel is dropped in the reaction medium, N_2 adaptor is placed on the neck again and reaction proceeds for 24 hours and reaction proceed like in Fig. 2.

After reaction, hot dichloromethane (DCM) is added in order to eliminate pyridium chloride for purification. Then, reaction mixture was extracted by 5% HCl (Sigma Aldrich) solution and 10% $NaHCO_3$ (Tekkim) solution, respectively. In order to crystallize the PSU-ThC, the extracted solution is washed with hot methanol. Finally, the thienyl (ThC) end-capped product was dried at 65°C in vacuum oven for 6 hours.

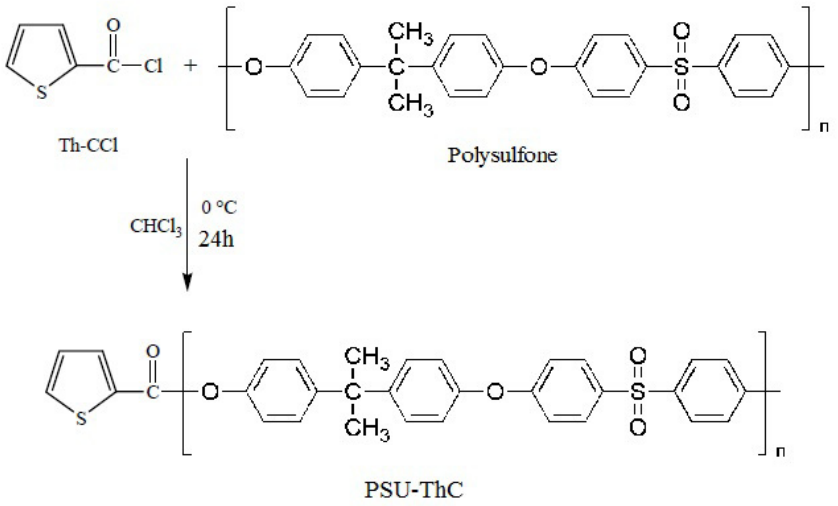

Fig. 2. End group functionalization of PSU with Th-CCl

2.4. Redox Copolymerization of PSU and PPy with Iron (III) Chloride

Copolymers of PSU-ThC and pyrrole were synthesized by chemical oxidative polymerization using iron (III) chloride as an oxidant. PSU-ThC served both as a macromonomer and acquires some of the polysulfone's good chemical and mechanical properties to the polypyrrole. Pyrrole and PSU-ThC amounts are taken according to the equation 3.

$$n_{Pyrrole} = 50 * n_{PSU-ThC} \quad (3)$$

PSU-ThC is taken 1g and dissolved with pyrrole in 40ml DMAC solvent and added into a beaker glass. The molar ratio of iron (III) chloride to pyrrole is determined by equation 4. Then FeCl3 mixture is prepared with 25ml DMAC.

$$n_{FeCl_3} = 2.4 * n_{Pyrrole} \quad (4)$$

FeCl3- DMAC mixture is given to the reaction mixture via a dropping funnel, about 10 minutes. The reaction took place at 25oC and lasted about 24 hours and reaction mechanism is like in Fig. 3. In the end of the reaction it can be observed that the color of reaction mixture is black and copolymer is soluble in its solvent.

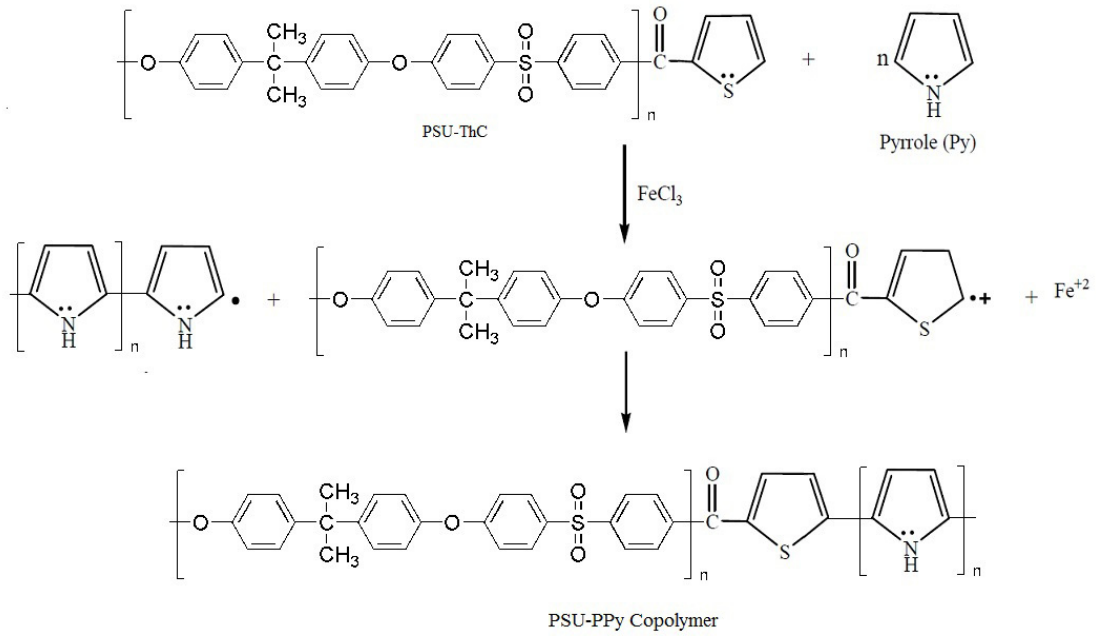

Fig. 3. Copolymerization of PSU-PPy

2.5. Analysis

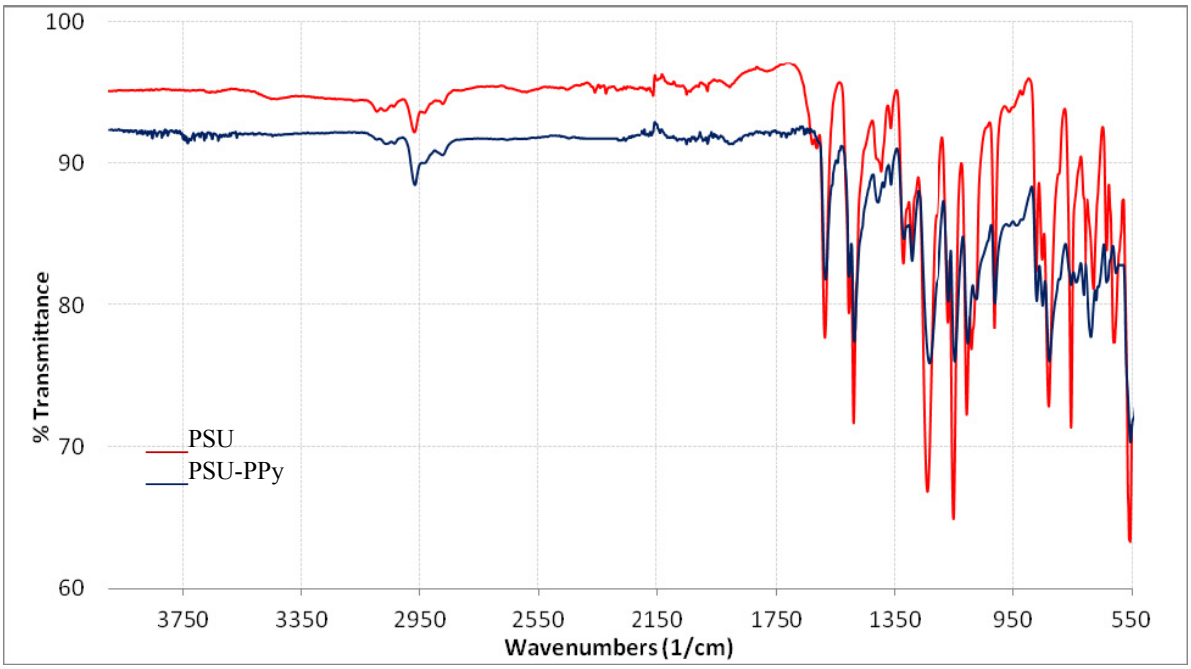

Fig. 4. FTIR results of PSU and PSU-PPy Copolymer

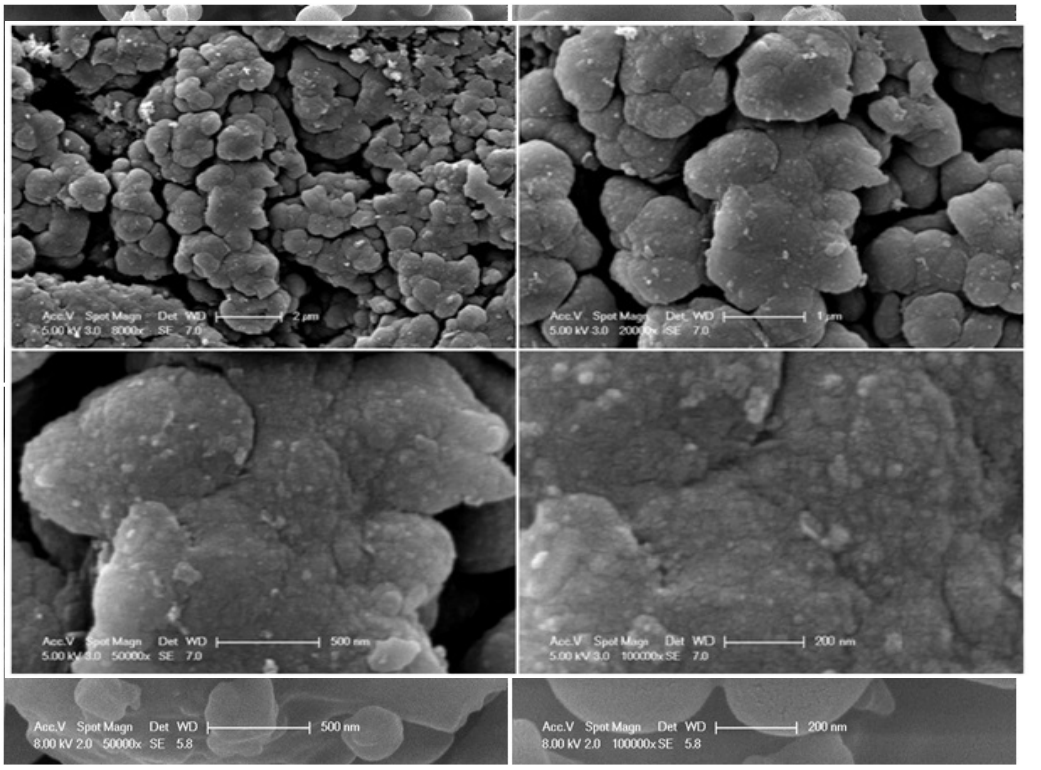

Fig. 5. SEM results of PSU

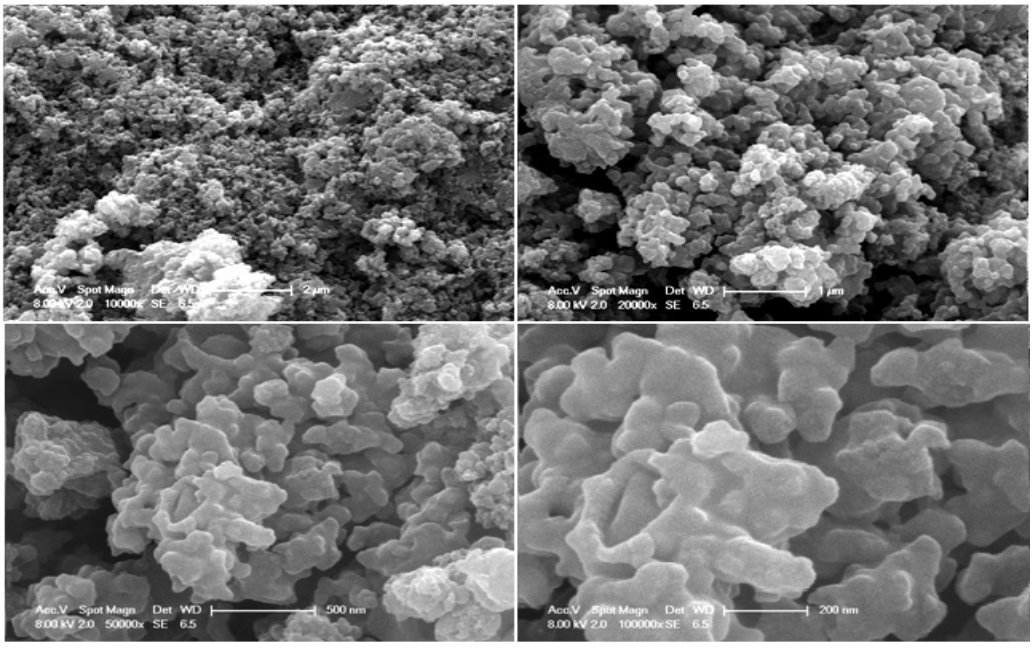

Fig. 6. SEM results of PPy PSU and PPy copolymer

The peak of the PSU-PPy around 1220cm-1 in Fig. 5, atributes the C-N screcthing band. In both FTIR peaks around 2950cm-1 is due to the aliphatic C-H bonds of the materials. The characteristic peaks of PPy in the PSU-PPY FTIR around 1540cm–1 and 1490cm–1 correspond to the C=C stretching, whereas peaks about 1670cm–1 and 1400cm–1 represent to respectively, C=N and C–N bonds. The occurrence of small peaks at PSU-PPy around 3700cm–1 is assigned to presence of N–H stretching vibrations. Most importantly the FTIR data of the PSU shows the ester carbonyl of the PSU peak at around 1750cm−1 and less broad peak at around 3400cm-1 indicate that small amount of hydroxy groups comes nonfunctionalized PSU. This weak OH peak disappears in the PSU-PPy copolymer FTIR, since PSU was thyenil end-capped and therefore reacted with pyrrole monomers.

In Fig. 5 and Fig. 6 SEM images of the PSU, PPy and PSU-PPy copolmer are shown respectively. These SEM results shows the particle images with the sizes of 2μm, 1μmi 500nm and 200nm. One can say that the PSU SEM shows more shperical particles, while PPy shows coral shaped big particles. And SEM of the copolymer consist combination of both shapes.

3. Conclusion

According to the SEM results of the PSU, PPy and PSU-PPy copolymer, one can that copolymer images both involves coral shape and particle shape arising from the polypyrrole and polysulfone polymers respectively. Also FTIR results promotes the copolymer existance. Consequently copolymer a new material having different properties and synthesis methods were combined in this paper's research. For further studies this material and its technique can be used for membrane production and applications.

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